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Anharmonic lifetime of H and D on the Si surface

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Abstract. The study of H and D adatoms on the surface of Si by STM technique and by optical measurements indicate that anharmonic interaction of adatom localized vibrations with surface phonons of Si defines both the absorption line width and the yield of the desorption. The anharmonic lifetime of H and D adatoms is calculated.

STM studies of the Si surface terminated by H or D demonstrated that the lifetime of D-adatom is much shorter than the lifetime of H-adatom. At the low level of the excitation, the desorption yield demonstrates the temperature dependence which indicates on the essential role of the H or D vibrational anharmonic lifetime in the process of desorption [1].

The study of IR absorption by stretching localized vibrations of H adatoms on the surface Si (111) [2] has demonstrated the anomalous temperature dependence of the integrated absorption. The line intensity (integrated area) decreases by 20% as the temperature is raised above the temperature 130 K to 560 K. Authors of the paper [2] believe that the anomalous temperature dependence follows from the strong anharmonic interaction of H–Si stretching modes with H–Si bending mode.

All the facts of the case have something in common with those which were widely discussed in 60-es in connection with optical properties of U-center localized vibrations in alkali halides. It had been shown by Hughes [3] and Ipatova *et al.* [4] that anomalous temperature dependence of the integrated intensity can be understood to be due to the large difference of the localized frequency and the frequencies of the bulk modes of alkali halides (adiabatic approximation). It had been shown that the strength of the absorption by the localized mode has the exponential temperature dependence of the Debye–Waller type.

This paper deals with the theory of anharmonic line width and integrated absorption by localized vibrations of H- or D-adatoms on the surface of Si (111). The anharmonic interaction of Si–H stretching localized mode with the substrate vibrational Si modes is taken into account. Since the Si–H stretching mode frequency is $\omega_{\text{loc}}(\text{H}) = 2085 \text{ cm}^{-1}$, stretching mode frequency of Si–D is 1516 cm^{-1} [5], and the maximum phonon frequency of Si is $\omega_L(\text{Si}) = 514 \text{ cm}^{-1}$, the adiabatic parameter,

$$\lambda = \frac{\omega_L}{\omega_{\text{loc}}} < 1, \quad (1)$$

holds for both H–Si and D–Si adatoms. It means that due to anharmonic interaction the slow motion of Si-atoms occur in an averaged field of fast vibrations of light adatom. It is shown that there appear static displacements of Si atom equilibrium sites. Vibrations of the Si atoms occur about new equilibrium positions.

The shift of equilibrium positions results in the exponential temperature dependent factor, Debye–Waller factor, in both the integrated absorption and in the spectral line width of the light absorption by localized vibrations of the H or D adatoms. This exponential

factor depends on the temperature and on the mass of adatom. It is different for the localized vibrations of isotope complexes Si-H or Si-D.

We assume that the adatom (H or D) of the mass M' is situated on the (111) surface of Si. Adatom is supposed to be bound by the force constant in the “on-site” configuration to the surface atom of Si at the lattice site $l = (l_x l_y l_z) = (000) \equiv 0$. The position of adatom is $l = (001) \equiv 1$. The mass of the Si atom is M .

The coefficient of the absorption of IR light at frequencies $\omega \approx \omega_{\text{loc}}$ has the form [6]

$$K(\omega) = -c_d \frac{e^2}{\hbar v_0} \text{Im} D_{\alpha\beta}^R(1, 1; \omega) \frac{E_\alpha E_\beta}{E^2}, \quad (2)$$

c_d being the surface concentration of adatoms, v_0 is the volume of the crystal primitive cell and $D_{\alpha\beta}^R(1, 1; \omega)$ is the one-particle retarded Green's function of the adatom localized vibrations.

The retarded Green's function $D_{\alpha\beta}^R(1, 1; \omega)$ can be calculated by the temperature Green's function technique. The temperature Green's function $D_{\alpha\beta}(1, 1; i\omega_n)$ with $\omega_n = 4\pi nT/\hbar$ satisfies Dyson equation

$$D_{\alpha\beta}(1, 1; i\omega_n) = D_{\alpha\beta}^{(0)}(1, 1; i\omega_n) + \sum_{ls, l's'} D_{\alpha\gamma}^{(0)}(1, ls; i\omega_n) \Pi_{\gamma\delta}(ls, l's'; i\omega_n) D_{\delta\beta}(l's', 1; i\omega_n), \quad (3)$$

where $ls, l's'$ are positions of the crystal lattice sites; $\Pi_{\gamma\delta}(ls, l's'; i\omega_n)$ is the polarization operator produced by anharmonic terms in the potential energy of the system. Taking into account the square symmetry of the adatom position on the surface, one can find $D_{\alpha\beta}(1, 1; i\omega_n) = D(1, 1; i\omega_n)\delta_{\alpha\beta}$ and $\Pi_{\alpha\beta}(1, 1; i\omega_n) = \Pi(1, 1; i\omega_n)\delta_{\alpha\beta}$.

Adiabatic parameter, Eq. (1), allows to neglect in the sum over $(ls, l's')$ in Eq. (3) non diagonal terms $D(1, ls; i\omega_n)$ and to find $D(1, 1; i\omega_n)$ from algebraic equation. The retarded Green's function $D^R(1, 1; \omega)$ is the analytic continuation in ω of temperature Green's function $D(1, 1; i\omega_n)$. One can separate in $\Pi(1, 1; \omega)$ the real and the imaginary parts, $\Pi(1, 1; \omega) = \Delta(1, 1; \omega) - i\Gamma(1, 1; \omega)$, which are in charge of the anharmonic shift $\text{Re}\Pi \equiv \Delta(1, 1; \omega)$ of localized frequency and the decay of the localized vibration $\text{Im}\Pi \equiv \Gamma(1, 1; \omega)$.

The quantity $\Gamma(1, 1; \omega)$ is defined by the processes which satisfy the conservation laws of the energy and the momentum. When the third order anharmonic term is taken into account, in the first approximation of the perturbation expansion, $\Gamma(1, 1; \omega_{\text{loc}})$ does not vanish only when $\omega_L < \omega_{\text{loc}} < 2\omega_L$. The condition holds neither for H- nor for D-adatoms. In order to find $\Gamma(1, 1; \omega)$ the anharmonic terms of the 4th order should also be taken into account. There are no limitations of this type for the shift $\Delta(1, 1; \omega)$: all possible virtual anharmonic phonon processes contribute to Δ . As a result, $\Delta(\omega) > \Gamma(\omega)$ and the shift Δ is defined by the third order anharmonicity. The expansion of $\Pi(1, 1; \omega)$ near $\omega \approx \omega_{\text{loc}}$ gives

$$D^R(1, 1; \omega) = \frac{1}{1 - \Delta'(\omega_{\text{loc}})} \left(\frac{\hbar}{M'} \right) \frac{1}{\omega - \omega_c(T) + i\gamma(\omega)}, \quad (4)$$

where

$$\omega_c^2(T) = \omega_{\text{loc}}^2 + \frac{\Delta(\omega_{\text{loc}})}{1 - \Delta'(\omega_{\text{loc}})} \quad \text{and} \quad \gamma(T) = \frac{\Gamma(\omega_{\text{loc}})}{1 - \Delta'(\omega_{\text{loc}})}. \quad (5)$$

Here $\Delta'(\omega_{\text{loc}}) = \left(\frac{d\Delta}{d\omega^2} \right)_{\omega^2=\omega_{\text{loc}}^2}$.

Calculations of polarization operator $\Pi(1, 1; \omega)$ and corresponding ω_c and γ with the help of the temperature Green's function technique allow to use the parameter Eq. (1) and to find the main contribution to $K(\omega)$

$$K(\omega) = c_d \frac{e^2}{\hbar v_0} \left(\frac{\hbar}{2M' \omega_{\text{loc}}} \right) e^{-2W(T)} \frac{e^{-2W(T)} \Gamma}{(\omega - \omega_c)^2 + (e^{-2W(T)} \Gamma)^2}. \quad (6)$$

Here the quantity $W(T)$ is defined by the 3rd order anharmonic terms $\Phi^{(3)}$

$$2W(T) = \sum_{\lambda} \frac{\hbar}{2M \omega_{\lambda}} \left(\frac{\hbar}{2M' \omega_{\text{loc}}} \right)^2 \left| \Phi^{(3)} \right|^2 \frac{(2N_{\lambda} + 1)}{(\hbar \omega_{\lambda})^2}, \quad (7)$$

where ω_{λ} , N_{λ} are the normal mode frequencies and the occupation phonon numbers of vibrations in semi-infinite Si, $\Phi^{(3)}$ is the closure of the anharmonic force constants with the phonon polarization vectors.

It follows from Eq.(6) that the quantity $e^{-2W(T)} \Gamma(\omega_{\text{loc}})$ is the line width of optical absorption by high frequency localized mode. At low temperatures $T < \Theta_D$, Θ_D being Debye temperature, the factor e^{-2W} does not depend on temperature: $e^{-2W(0)} = \text{const}$. At high temperatures $T > \Theta_D$ the Debye–Waller factor is the linear function of temperature.

Two contributions to the quantity Γ are known: the relaxation, Γ_1 , and the dephasing, Γ_2 . At low temperatures $T < \Theta_D$, the main contribution to the line width for H adatom $\Gamma(\text{H})$ is shown to come from dephasing mechanism of broadening. $\Gamma_2(\text{H})$ is vanishing as $e^{-(\hbar \omega_{\lambda}/T)}$ at $T \rightarrow 0$. In case of D-adatom, the dephasing Γ_2 defines the line width in the temperature interval $T > T_1$ only. At $T = T_1 \approx 60$ K. the relaxation broadening $\Gamma_1(\text{D})$ becomes more important.

At low temperatures $T < \Theta_D$, the comparison of the line width for H- and D-adatoms shows that at $T > T_2 \approx 30$ K the main mechanism of broadening is dephasing Γ_2 for both H- and D-adatoms. Order of magnitude evaluation shows that $\Gamma_2(\text{H}) > \Gamma_2(\text{D})$. At $T \leq T_2$ the relaxation broadening $\Gamma_1(\text{D})$ becomes more important for D-line width and H-line width becomes less than D-line width: $\Gamma_2(\text{H}) < \Gamma_1(\text{D})$. At high temperatures $T > \Theta_D$, the temperature dependence of the broadening is defined by $\Gamma(T) e^{-2W(T)}$ where $\Gamma(T)$ is dephasing process for both H- and D-adatoms. Numerical evaluations shows that at $T \geq 250$ K, the relaxation between the line widths, $\Gamma(\text{D}) e^{-2W(\text{D})} > \Gamma(\text{H}) e^{-2W(\text{H})}$, holds due to exponential factor.

The integrated absorption is equal to

$$J = \int_0^{\infty} d\omega K(\omega) = c_d \frac{e^2}{\hbar v_0} \left(\frac{\hbar}{2M' \omega_{\text{loc}}} \right) e^{-2W(T)}. \quad (8)$$

It follows from Eq. (8) that the integrated intensity J has exponential temperature dependence which is stronger in case of H-adatom than for D-adatom. Order of magnitude evaluation has shown that $J(\text{H}) \approx 2J(\text{D})$ what is in the good agreement with experimental data from [6] where $J(\text{H}) = 1.9J(\text{D})$ is obtained.

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